Kinetics and mechanism of the reduction of enneamolybdonickelate(IV) by sulfite

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The kinetics and mechanism of the reduction of enneamolybdonickelate(IV) by sulfite in acetic acid-ammonium acetate buffer solution was studied by spectrophotometry. The reaction rate law is $-\frac{dc_{Ni^{IV}M}}{d_t} = \frac{kK[H^+]_e[SO_3^{2-}]_T[Ni^{IV}M]_T}{K[H^+]_e[SO_3^{2-}]_T + K_{a1} + [H^+]_e} = k_{obs}[Ni^{IV}M]_T$. The rate constants and activation parameters of the rate-determining step were evaluated. A mechanism for this reaction is proposed.

Keywords: enneamolybdonickelate(IV) sulfite kinetics and mechanism redox reaction

Heteropolyacids and their salts are known as acidic and redox catalysts in some reactions.[1–3] Studies on the kinetics and mechanism of redox reactions of heteropolyacids and their salts are important because of the use of these compounds as redox reaction catalysts. However, most authors have paid attention to studying the catalytic activities of heteroployacids and their salts that have Keggin and/or Dawson structures,[4–7] in which the heteroatom is coordinated to four oxygen atoms in a tetrahedral arrangement. Few papers have reported on other types of heteropolyanions applied as catalysts. Ammonium enneamolybdonickelate(IV) {$(NH_4)_6[NiMo_9O_{32}]6H_2O$} is a Waugh-type heteropolyacid salt in which nickel is coordinated to six oxygen atoms in a slightly distorted octahedral arrangement. Each of these oxygen atoms is coordinated to three molybdenum atoms and each molybdenum atom is also surrounded by six atoms though in a very distorted octahedral geometry. It can oxidise substances, including organic and inorganic reagents.[8] Very few references to the kinetics and mechanism of this type of heteropolyacid salts have been found. A study on the kinetics and mechanism of the reduction of enneamolybdomanganate(IV) by sulfite may throw some light on Waugh-type of heteropolyacids and their salts as catalysts.

Experimental

Materials

Ammonium enneamolybdonickelate(IV) ($Ni^{IV}M$) was prepared by the method described earlier.[9] The $Ni^{IV}M$ concentration of solution was 1.036×10^{-3} mol/l. A solution of ammonium sulfite (AR) was prepared by direct weighing, and its purity was checked by a titration method. The concentration of sulfite in this solution was 1.666×10^{-1} mol/l and solutions of sulfite of different concentation were prepared by diluting it with water. The buffer solution of acetic acid-ammonium acetate was prepared by adding acetic acid in ammonium acetate solution and adjusting to the pH value given. The total concentration of the buffer was approximate 0.5 mol/l. Ammonium nitrate was used to adjust the ionic strength.

Test for free radicals

Generation of free radicals during the course of the reaction was confirmed by polymerisation of acrylonitrile (AR) in the solution. No white curdy precipitate was produced after adding a certain amount of acrylonitrile after 30 minutes.

Kinetic measurements

Kinetic measurements were made on a UV-265 spectrophotometer equipped with a thermostatic cell holder. The appropriate amount of oxidative solution was added to the buffer solution. The reductive solution was then added and the two kinds of solutions were placed in the thermostatic bath of spectrophotometer. The reaction rates were determined by observing the decrease in absorption at 564 nm, the maximum absorption of $Ni^{IV}M$ solution, under the condition in which the concentration of $SO_3^{2-}$is in large excess over that of $Ni^{IV}M$. The temperature of the reaction was controlled to 293±0.10K. The pH value was measured by a pHS-2 pH-meter of. Blank experiments were run with no sulfite reducing agent, a known amount of ammonium nitrate/acetate buffer, to check that there was no reduction of the $Ni^{IV}M$ oxidant by ammonium or acetate in absence of sulfite. All experiments were carried out in a 99.9% nitrogen gas atmosphere.

Determination of reaction products

The reaction products were obtained by mixing 1:1 oxidant and reductant in buffer solution then measuring the UV and IR spectra. They confirmed that the reaction products are $Ni^{II}Mo_6O_{24}^{10-}$ and SO_4^2.

Results and discussion

The order of the reaction: dependence on $Ni^{IV}M$

The (A_t–A_∞) values were obtained from curves of absorbance (A_t) versus time (t) of the reaction of $Ni^{IV}M$ with sulfite. The values of $\ln(A_t–A_\infty)$ *versus* time are plotted in Fig.1. It can be seen that $\ln(A_t–A_\infty)$ *versus t* is linear. Therefore, pesudo-first-order reaction dependence on [$Ni^{IV}M$] was confirmed.

Determination of the order of the reaction: dependence on sulfite

For a given $Ni^{IV}M$ concentration, temperature, pH and ionic strength, the rates ($-d_{cNiIVM}/d_t$) can be obtained from the A_t/t curves of reaction between $Ni^{IV}M$ and different concentrations of sulfite. A plot of $\ln(-d_{cNiIVM}/d_t)$ against ln SO_3^2 is not good line. The slope of this line is –0.15. Therefore, a fractional order reaction with respect to sulfite is indicated by the slope of the line. Dependence of on SO_3^2 is shown in Fig.2. It can be seen that relationship between $\frac{[SO_3^{2-}]}{k_{obs}}$ $\frac{[SO_3^{2-}]}{k_{obs}}$ and SO_3^2 is linear.

Effect of [H⁺] on the reaction

For a given concentration of [SO_3^2], $Ni^{IV}M$, temperature and ionic strength $\lg(-d_{cNiIVM}/d_t)$ dependence on $\lg[H^+]$ is linear in the pH range of 3.8–4.9 and the slope of the line is 0.66, which indicates that the reaction with respect to [H^+] is a fractional order. This means that [H^+] is in the numerator and the denominator in the fraction. Various fractional orders with respect to [H^+] were tried. A plot of $\frac{1}{k_{obs}}$ against against $\frac{1}{[H^+]}$ is liners (see Fig.3). In this pH range the main species is HSO_3^- based on K_a values forH_2SO_3.

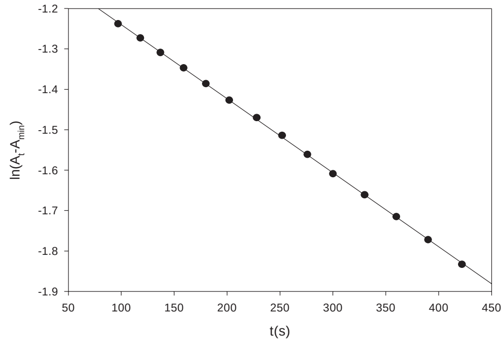

Fig. 1 Dependence of $\ln(A_t–A_\infty)$ on *t*. [$Ni^{IV}M$]=0.5018mol/L, [SO_3^{2-}]=0.0833mol/L, pH=4.20, *T*=293.0K.

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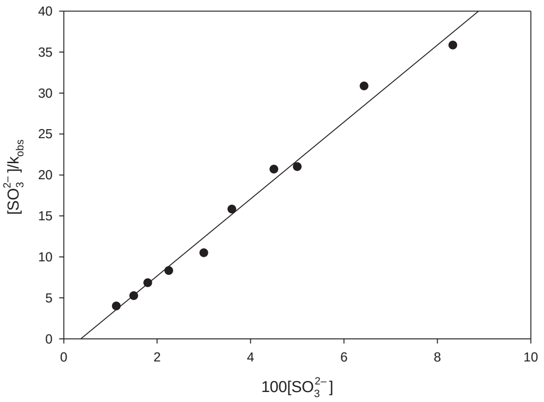

Fig. 2 Relation between reaction rate constant (k_{obs}) and concentration of sulfite($[SO_3^{2-}]$) pH=4.20 T=293.0K.

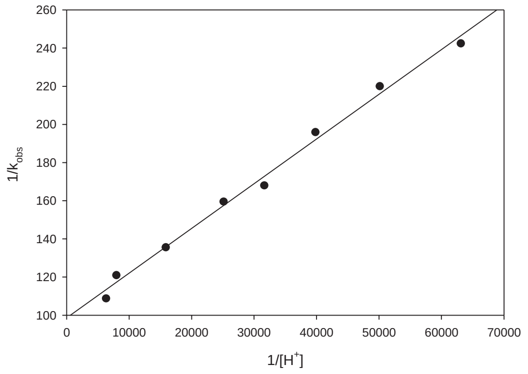

Fig. 3 Plot of $\frac{1}{k_{obs}}$ versus $\frac{1}{[H^+]}$, T=293.0K.

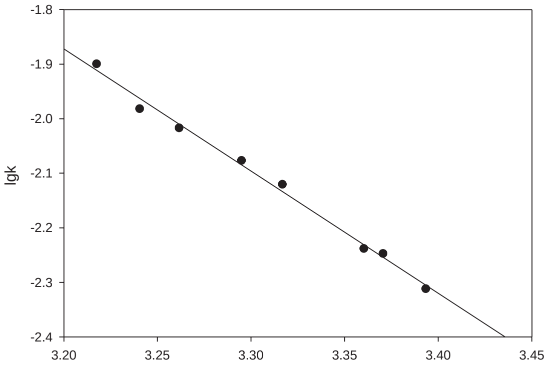

Fig. 4 Dependence of lg$k$ on $1/T$.

Proposal of the reaction mechanism

Based on the experimental results a reaction mechanism was proposed as follows:

$$H^+ + SO_3^{2-} \xrightleftharpoons{1/K_{a2}} HSO_3^- \qquad (1)$$

$$H^+ + HSO_3^- \xrightleftharpoons{1/K_{a1}} H_2SO_3 \qquad (2)$$

From. the disassociation equilibria of Eqns (1) and (2), the following relationships can be derived:

$$[HSO_3^-]_e = \frac{[H^+]_e[SO_3^{2-}]_e}{K_{a2}} \qquad (3)$$

$$[H_2SO_3]_e = \frac{[H^+]_e^2[SO_3^{2-}]_e}{K_{a1}K_{a2}} \qquad (4)$$

$$Ni^{IV}M + H_2SO_3 \xrightleftharpoons{K} Ni^{IV}M * H_2SO \qquad (5)$$

$$K = \frac{[Ni^{IV}M * H_2\dot{S}O_3]_e}{[Ni^{IV}M]_e[H_2SO_3]_e} \qquad (6)$$

$$[SO_3^{2-}]_T = [SO_3^{2-}]_e + [HSO_3^-]_e + [H_2SO_3]_e + [Ni^{IV}M * H_2SO_3]_e \quad (7)$$

where e represents equilibrium.

The value of $[Ni^{IV}M * H_2SO_3]_e$ can be neglected because the value of $[SO_3^{2-}]_T$ is in large excess over that of $[Ni^{IV}M]$. Therefore Eqn (7) can be described as follows:

$$[SO_3^{2-}]_T = \frac{K_{a1}K_{a2} + K_{a1}[H^+]_e + [H^+]_e^2}{[H+]_e^2} \qquad (8)$$

$$[H_2SO_3]_e = \frac{[H^+]_e^2[SO_3^{2-}]_T}{K_{a1}K_{a2} + K_{a1}[H^+]_e + [H^+]_e^2} \qquad (9)$$

$$[Ni^{IV}M]_T = [Ni^{IV}M]_e = [Ni^{IV}M * H_2SO_3]_e = \frac{1 + K[H_2SO_3]_e}{K[H_2SO_3]_e}[Ni^{IV}M * H_2SO_3] \qquad (10)$$

where T represents the total.

From Eqns (9) and (10) following equation can be obtained:

$$[Ni^{IV}M * H_2SO_3]_e = \frac{K[H^+]_e^2[SO_3^{2-}]_T[Ni^{IV}M]_T}{K[H^+]_e^2[SO_3^{2-}]_T + K_{a1}K_{a2} + {}^2K_{a1}[H^+]_e + [H^+]_e} \quad (11)$$

The value of $K_{a1}K_{a2}$ can be neglected because it is small value in the experimental range. The following can be obtained from Equ(11):

$$[Ni^{IV}M * H_2SO_3]_e = \frac{K[H\ \ ]_e[SO_3^{2}\ \ ]_T[Ni^{IV}M]_T}{K[H^+]_e[SO_3^{2-}]_T + K_{a1} + [H^+]_e} \qquad (12)$$

$$Ni^{IV}M * H_2SO_3 + 5H_2O \xrightleftharpoons{Slow.......k} Ni^{II}M'H_6 + SO_4^{2-} + 3HMoO_4^- + 3H^+ \qquad (13)$$

where $Ni^{II}M$ represents $Ni^{II}Mo_6O_{24}^{10-}$.

$$\frac{d_{C_{Ni^{IV}M}}}{d_t} = k[Ni^{IV}M * H_2SO_3]_e = \frac{kK[H^+]_e[SO_3^{2-}]_T[Ni^{IV}M]_T}{K[H^+]_e[SO_3^{2-}]_T + K_{a1} + [H^+]_e} \quad (14)$$

where

$$k_{obs} = \frac{Kk[H^+]_e[SO_3^{2-}]_T}{K[H^+]_e[SO_3^{2-}]_T + K_{a1} + [H^+]_e} \qquad (15)$$

Rewriting equation (15) we can obtain follow expression:

$$\frac{[SO_3^{2-}]_T}{k_{obs}} = \frac{[SO_3^{2-}]_T}{k} + \frac{K_{a1}}{Kk[H^+]} + \frac{1}{Kk} \qquad (16)$$

These equations agree with experimental data.

Evaluation of the activation energy and the activation parameters

Dependence of the rate constants on the temperature (T) can be obtained from the curves of absorbance versus temperature under the condition of given values of $[Ni^{IV}M]$, $[HSO_3^-]$, ionic strength and pH. Keeping the same conditions as above and only changing the pH value, another set of values for k_{obs} dependence on temperature can be obtained, see Table 1. From the data in Table 1 it can be seen that k_{obs} decreases with pH value at a given temperature. This result agrees with that of the effect of $[H^+]$ on the rate. Based on Eqn (16) and data in Table 1 we can obtain the values of k at different temperatures, see Table 1. Fig.4 shows the 1gk dependence on $\frac{1}{T}$. It can be seen that the relationship between 1gk and $\frac{1}{T}$ is linear. The activation energy of the

Table 1 Values of k_{obs} and k at different temperature and pH

T/K	pH	10^3k_{obs}	10^3k	$[SO_3^{2-}]$/mol l^{-1}
294.7	3.80	3.65		
	4.20	2.65	4.88	0.021
296.7	3.80	4.73		
	4.20	3.80	5.66	0.021
297.6	3.80	4.96		
	4.20	4.10	5.78	0.021
301.5	3.80	6.62		
	4.20	5.57	7.58	0.021
303.5	3.80	7.62		
	4.20	6.71	8.38	0.021
306.6	3.80	8.81		
	4.20	7.83	9.62	0.021
308.6	3.80	9.90		
	4.20	9.20	10.43	0.021
310.8	3.80	12.20		
	4.20	11.64	12.61	0.021

rate-determining step of the reaction (E_a) can be obtained from the slope of the line. The activation energy, E_a, is 43.26 kJ/mol at 293±0.1 K, based on the equations $E_a = \Delta H^{\neq} + RT$ and $\Delta S^{\neq} = R[10g\ A - 10g \frac{k_BT}{h} \frac{1}{2.303}] \times 2.303$, where lgA is the intercept on the *lgk* axis in Fig.4, and k_B, h and R have their usual significances. The activation parameters can be calculated. Therefore, the activation enthalpy ($\Delta H^{\neq}$) and activation entropy ($\Delta S^{\neq}$) of the rate-determining step of the reaction at 293±0.1K, are 40.83 kJ/mol and –135.02 J/mol K, respectively. The negative value of $\Delta S^{\neq}$ in the rate-determining step of the reaction may be attributed to the joint effect of ionic complexity decrease and hydration degree decrease.

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